

Choice of electrode geometry for accurate measurement of organic photovoltaic cell performance

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The relationship between the performance and the electrode geometry of organic photovoltaic devices was investigated to establish the proper electrode geometry for reproducible and accurate performance measurement. Photovoltaic cells (ITO/PEDOT:PSS/P3HT+PCBM/LiF/Al) having crossbar-type and island-type electrode geometries were fabricated. The crossbar-type cells varied greatly in performance depending on the illuminated light beam size relative to the overlap area of the crossbar-type electrodes due to excess photocurrent generated from the cell region outside the overlapped electrode area, where PEDOT:PSS serves as anode. We systematically investigated the relationship between the conductivity of the PEDOT:PSS, the illumination area, and the amount of excess photocurrent generated. © 2008 American Institute of Physics. [DOI: 10.1063/1.2895058]

Organic photovoltaic cells (OPVCs) are one of the popular research areas and have been investigated intensively because of their unique advantages such as easy processability, light weight, and the flexibility in organic material design. Currently, the best power conversion efficiency (PCE) of OPVC is around 3.5%–6.5%.^{1–5} However, since at least 10% PCE should be achieved in order to commercialize OPVC, various efforts are in progress to achieve better performance. Heterojunction solar cells having controlled nanostructures have been investigated to increase the interface area between the donor and the acceptor in order to achieve efficient exciton dissociation and charge transport.^{6–8} Improving the energy harvesting capability of OPVC by developing low band gap conjugated molecules^{9,10} and by applying the surface plasmonic resonance concept¹¹ has also been actively investigated. Very recently, tandem cells composed of a front cell (Poly(3-hexylthiophene)(P3HT)/[6,6]-phenyl-C61-butyric acid methyl ester(PCBM)blend) and a back cell (infrared absorbing conjugated polymer/PCBM blend) were reported with 6.5% PCE and have opened a new strategy to achieve a higher PCE.¹

As the PCE is the representative parameter to evaluate the performance of photovoltaic (PV) cells, the measurement of this value should be accurate and reproducible in order that different devices can be compared on an equal basis.¹² However, in reality, it could be challenging to obtain precisely reproducible PCE even from cells having identical structure and composition because there are many subtle parameters such as annealing condition,^{2–4,13} solvent selection,¹⁴ and the presence of oxygen and moisture^{10,15,16} in the device fabrication steps and during the device characterization steps. Moreover, there are no standardized device size and structure, illumination condition, and characterization methods of OPVC. Two types of electrode configuration are often used in making OPVCs: a

crossbar-type and an island-type electrode. In this work, we systematically investigated the effects of the electrode geometry combined with illumination condition on the PCE of organic solar cells. We fabricated PV (Indium tin oxide(ITO)/Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)(PEDOT:PSS)/P3HT+PCBM/LiF/Al) using both aforementioned electrode configurations. The patterned crossbar-type electrode geometry is the most commonly used configuration for organic light emitting diodes (OLEDs) because this structure allows conveniently addressing individual pixels. The same crossbar-type electrode geometry has been adapted to OPVC fabrication for the same convenience. However, we found that the crossbar-type electrode geometry can lead to an incorrect analysis of PCE of the OPVCs even though it is an acceptable structure for OLED. While the cells having the island-type electrode geometry gave a consistent cell performance, the performance of the crossbar-type cells varied greatly depending on the size of the illuminated light beam on the cells relative to the overlapped area of the crossbar electrodes. When the

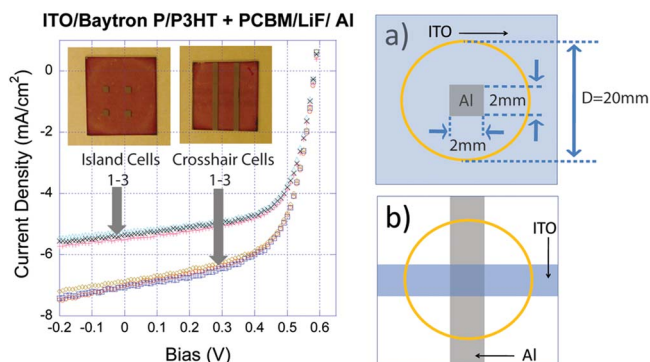


FIG. 1. (Color online) J - V curves of OPVCs having (a) island-type electrode geometry and (b) crossbar-type electrode geometry (illumination diameter: 20 mm, intensity: AM1.5G 100 mW/cm²). For the device characterization having the island-type electrode, the anode contact was made using a probe and the cathode contact was made using a gold wire.

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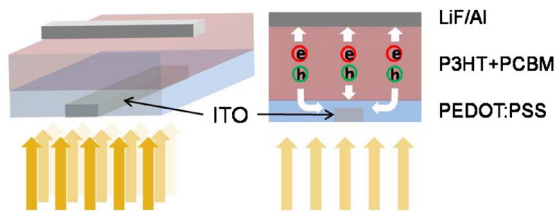


FIG. 2. (Color online) Left: Characterization scheme of OPVC having crossbar-type electrode geometry under illumination larger than the overlapped area of the crossbar-type electrodes. Right: Excess current generation in PEDOT:PSS||Al device where there is no ITO.

illuminated area was larger than the overlapped area of the crossbar electrodes, excess photocurrent was generated from the parasitic OPVC regions outside of the overlap area, where there was no ITO electrode because the conductive PEDOT:PSS layer plays the role of an effective anode.

Figure 1 shows the structure of the crossbar-type cell and the island-type cell having an identical overlapped area of $2 \times 2 \text{ mm}^2$ between the ITO anode and the Al cathode. To make the island-type PV cells, a PEDOT:PSS layer of 65 nm was spin coated onto an ITO slide followed by P3HT/PCBM blend deposition (blend ratio 1:1, thickness: 150 nm) by spin casting. A 1-nm-thick LiF layer and a 100-nm-thick Al layer were deposited subsequently through a shadow mask to form a $2 \times 2 \text{ mm}^2$ area cathode. The crossbar-type PV cells had the same composition and layer thicknesses, but used patterned ITO and Al electrodes as shown in Fig. 1(b). We analyzed the cell performance by illuminating AM 1.5 G simulated sunlight (Oriol Solar Simulator, 100 mW/cm^2) on the PV cells. The beam diameter of the simulated sunlight on the device surface was 20 mm, and the intensity of the light was uniform throughout the area. In principle, we should expect to obtain the same cell performance from the two different types of PV cells. However, our measurements of the cell performances between the PV cells having the two different electrode geometry were consistently different. While the measured short circuit current density (J_{sc}) of the island-type PV cells was 5.5 mA/cm^2 , the J_{sc} of the crossbar-type PV cells was much larger ($\sim 7 \text{ mA/cm}^2$). Multiple PV cells having the same electrode geometry of either type showed less than 5% variation in their PCE as shown in Fig. 1.

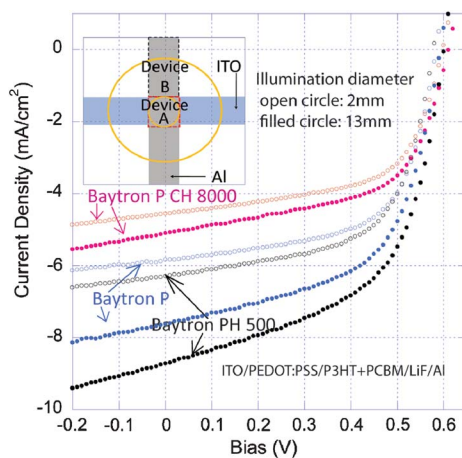


FIG. 3. (Color online) J - V curves of devices having crossbar-type electrode geometry. Three devices having different PEDOT:PSS—Baytron P CH 8000, Baytron P, and Baytron PH 500—were built and characterized under illumination by varying the beam diameter (beam diameters: 2 and 13 mm). Downloaded 31 Mar 2008 to 141.212.131.186. Redistribution subject to AIP license or copyright; see <http://apl.aip.org/apl/copyright.jsp>

TABLE I. Illumination area dependence of OPVCs ($2 \times 2 \text{ mm}^2$) having crossbar-type electrode geometry.

PEDOT:PSS	Beam diameter	2 mm	3.5 mm	5 mm	13 mm
Baytron P CH 8000 10^{-4} – 10^{-5} S/cm	J_{sc} (mA/cm ²)	4.57	4.95	5.11	5.11
	FF	0.59	0.57	0.56	0.56
	PCE (%)	1.63	1.71	1.77	1.78
Baytron P 0.1–1 S/cm	J_{sc} (mA/cm ²)	5.84	7.1	7.58	7.64
	FF	0.61	0.58	0.57	0.56
	PCE (%)	2.1	2.4	2.57	2.56
Baytron PH 500 10 – 10^2 S/cm	J_{sc} (mA/cm ²)	6.29	7.05	8.65	8.72
	FF	0.60	0.56	0.54	0.54
	PCE (%)	2.2	2.36	2.81	2.86

We hypothesized that the excess photocurrent of the crossbar-type cells is because the conducting PEDOT:PSS layer near the overlapped electrode region also collected photogenerated holes from the area where there is no ITO, as illustrated in Fig. 2. To verify this hypothesis, we investigated the relationship between the conductivity of the PEDOT:PSS and the excess photocurrent. We used three different conducting PEDOT:PSS materials—Baytron P CH 8000 ($\sigma=10^{-4}$ – 10^{-5} S/cm), Baytron P ($\sigma=0.1$ –1 S/cm), and Baytron PH 500 ($\sigma=10$ –100 S/cm)—and made identical crossbar-type cells. The cell performance was characterized by varying the illuminated beam sizes (beam diameters of 2, 3.5, 5, and 13 mm) of AM 1.5 G simulated sunlight (Fig. 3 and Table I). A few effects were observed. First, we illuminated only the overlapped electrode area by a 2.0 mm beam and found that the J_{sc} values increased with the conductivity of PEDOT:PSS. Second, with increased beam size, excess photocurrent was observed in all the crossbar-type PV cells until it eventually saturated, and the amount of the excess photocurrent increased with the PEDOT:PSS conductivity. We plotted the excess photocurrent against the size of the exposed area by subtracting the overlapped electrode region in Fig. 4. As shown in the figure, the excess current saturated when the excess exposed area outside of the electrode overlap [device B in Fig. 3 (inset)] was 5 mm^2 . This indicates

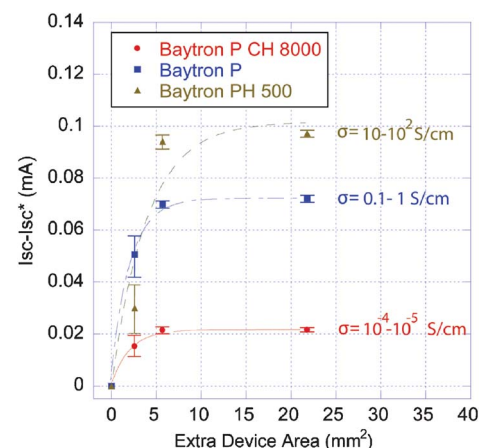


FIG. 4. (Color online) The plot of excess current ($I_{sc} - I_{sc}^*$) from PEDOT:PSS||Al device vs extra device area of PEDOT:PSS||Al device. I_{sc} : total current from organic photovoltaic cells having crossbar-type electrode geometry, I_{sc}^* : current generated from ITO||Al device. The lines are guides for the eyes.

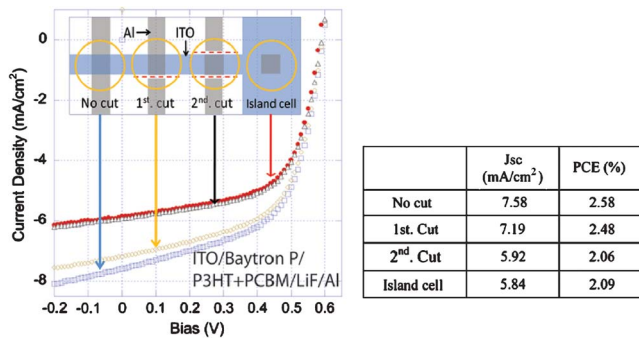


FIG. 5. (Color online) J - V curves of organic photovoltaic cells having crossbar-type electrode geometry as the aluminum cathode was cut to remove excess current from PEDOT:PSS||Al device. (Illumination diameter: 13 mm, intensity: AM1.5G 100 mW/cm².)

that only the PEDOT:PSS close to the edge of the ITO electrode can collect charges and contribute to excess current, and the amount of the excess current is proportional to the conductivity of PEDOT:PSS.

Based on the experimental results, we can consider that the crossbar-type cells are composed of two types of PV cells connected in parallel. One is the PV cell having ITO anode and Al cathode [i.e., device A in Fig. 3 (inset)] and the other is device B in Fig. 3 (inset) that has PEDOT:PSS as an effective anode instead of ITO. We built PEDOT:PSS (Baytron P)/P3HT+PCBM/LiF/Al PV cells on a glass substrate without ITO to mimic device B in Fig. 3 (inset). The devices, indeed, showed photovoltaic characteristic, but with a fill factor (FF) of only 0.25, which is much smaller than the FF of 0.61 of the equivalent device having ITO. This also explains why the FF of the crossbar-type PV cells decreased when the illuminated beam size increased, while the J_{sc} increased due to the contribution of device B to the total measured J_{sc} . In order to directly confirm that the excess current is from the parasitic PEDOT:PSS||Al device (device B), we built a crossbar-type PV cell (ITO/Bytron P/P3HT+PCBM/LiF/Al) and illuminated the PV cell with a beam of diameter 13 mm. We measured the J - V curves as we cut the Al cathode right next to the overlapped region, as illustrated in Fig. 5. Cutting the Al cathode removes the contribution of the parasitic PV cell (i.e., device B). As we can see from Fig. 5, as the Al cathode was cut into the 2×2 mm² square shape, the J_{sc} and PCE decreased, while the FF increased. After the second cut, the J - V curve of the crossbar-type PV cell became essentially the same as that of the island-type PV cell. We found the same effects from the crossbar-type PV cells made of Baytron P CH 8000 and Baytron PH 500.

To quantify the characteristic length of the parasitic device region that contributes to the excess photocurrent, we modeled the crossbar-type PV cell by a parallel connection of device A and a series of distributed PV cells of different distances (and, therefore, different resistances) to the biased ITO electrode. As the photogenerated holes collected by the PEDOT layer have to reach the ITO electrode to contribute to the measured photocurrent, the characteristic length of the parasitic device can be estimated by considering the voltage drop along the distance away from ITO device. The voltage drop can be expressed as $\Delta V = \int J_{ph} R_{sq} L dL$, where J_{ph} is the photocurrent, R_{sq} is the sheet resistance, and L is the distance of the parasitic element from the ITO electrode. The maximum distance can be estimated as $L_{max} = \sqrt{2\Delta V / J_{ph} R_{sq}}$, at

which the voltage drop is equal to the open-circuit voltage of the device and beyond which photogenerated holes can no longer contribute to the measured photocurrent. Based on the sheet resistance of the PEDOT material, our analysis showed this length to be ~ 400 μ m, which is in the same order of the lateral extension of the region outside the overlapped electrode, beyond which the measured excess current saturates.

To summarize our experiment, we found that the commonly used crossbar-type PV cells can produce a significant error in the PCE measurement if the beam diameter of the illuminated light is larger than the area of electrodes. The larger PCE observed using such a configuration is due to the excess photocurrent generated from the parasitic OPVC structure, where the conductive PEDOT layer acts as an effective anode.¹⁷⁻¹⁹ This can also explain why the excess photocurrent is proportional to the conductivity of the PEDOT:PSS layer and increases with the illuminated area. Two solutions are possible to prevent the error in characterization: either by making the area of light illumination equal to that of the active electrode area of PV cells or by using the island-type cathode design. Considering the technical difficulty of the former method, the latter approach is more convenient and practical.

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